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This invention relates to a process for the selective removal of H₂S from synthesis gas being rich in carbon monoxide and further containing hydrogen, carbon dioxide and optionally steam.

5 Selective removal is defined as a removal process being basically neutral with respect to the reactants contained in the synthesis gas, i.e. contents of other than impurities, steam and inert gas is not changed to any substantial degree. In addition, formation of components not already contained in the synthesis gas must be avoided.

10 H₂S and other sulphur compounds are poisonous to a wide range of catalysts e.g. nickel, iron and copper based catalysts used for synthesis in the industry. The catalysts are deactivated in contact with catalyst poisons contained in the gas. Sulphur compounds form stable compounds on the catalytic surface and block its active sites.

15 20 Therefore, selective removal of sulphur as defined above is industrially useful for removal of sulphur compounds downstream to reformers producing synthesis gas from hydrocarbons in chemical plants.

25 Examples, where downstream selective removal of sulphur compounds from synthesis gas is useful, include removal of H₂S and COS from synthesis gas generated in high temperature autothermal reformers. In an autothermal reformer sulphur may be acceptable in the hydrocarbon feed and all sulphur in the feed will be converted to H₂S and minor amounts of COS.

As the catalysts in the downstream synthesis section are susceptible to sulphur poisoning, sulphur must be removed to the low ppb level (<5 ppb). The sulphur removal is to be obtained either at inlet to the synthesis gas preparation section upstream to the reformer, or alternatively downstream to the reformer, in case the synthesis gas preparation section is tolerant to sulphur.

When downstream removal of sulphur compounds is applied, the removal process must fulfil certain requirements in terms of selectivity. In general it is not desired to change the composition of the synthesis gas generated, furthermore, components not already contained in the synthesis gas must not be formed.

When operating the removal process in praxis, selective removal of sulphur requires reduction of sulphur concentration to below 5 ppb in the treated synthesis gas. The removal process shall affect only impurities, steam and inert, and side-reactions are disadvantageous.

Synthesis gas generated in reformers comprises conventionally both substantial amounts of carbon monoxide, hydrogen, carbon dioxide, various inert compounds and impurities. In other applications synthesis gas is generated with very low levels of carbon dioxide, such as coal gasifiers. The synthesis gas to be treated by selective removal of sulphur is usually rich in carbon monoxide and further contains hydrogen, carbon dioxide and optionally steam.

The most conventionally used means of H₂S removal from a gas stream is passing the gas through a bed of zinc oxide

at elevated temperatures, typically from 300-450°C. Conventional zinc oxide absorbents are not useful in H₂S removal from wet synthesis gases being rich in carbon monoxide. Steam decreases the efficiency of H₂S removal through the absorption reaction



In wet synthesis gas sulphur content exceeds thus the sulphur limit of down stream catalysts. Further, ZnO absorbents are active catalysts in the water gas shift reaction at usual operating conditions.

Further common H₂S absorbents being based on nickel or copper, capable of reducing H₂S concentration to much lower levels cause unwanted side reactions like hydrocarbon formation, water gas shift and methanol synthesis.

EP 243,052 discloses agglomerates of copper and zinc and/or metals of Groups IIIA, IVA, VA, VIA and VIIA in form of oxides, hydroxides, carbonates and/or basic carbonates as useful sulphur absorbents in natural gas, NGL or liquid refinery products. Thereby, the treated fluids are preferably free of reducing gases.

We have found that unreduced basic carbonates are not useful in sulphur removal from synthesis gas, because basic carbonates are reduced by the reducing synthesis gas at temperatures as low as 55°C. At 40°C the reduction of the absorbent is absent or progresses very slowly, however, minor operational upsets will lead to temperature increments initiating the reduction process resulting in detrimental temperatures run-away.

US Patent No. 4,521,387 relates to sulphur absorbents in form of a Cu/ZnO catalyst, which is prepared by thermal decomposition of $Cu_xZn_y(OH)_6(CO_3)_2$. The absorbent is employed in deep purification of dry synthesis gas being free of carbon dioxide for the removal of e.g. H₂S and other impurities at a temperature of 100°C.

Undesired side-reactions during removal of sulphur from synthesis gas by use of the above absorbents are not discussed in EP 243,052 and US Patent No. 4,521,387.

It is generally known that the absorbent applied in US Patent No. 4,521,387 catalyses the production of methanol predominantly through the activation of CO₂.

It is also known that the absorbent applied to in JS Patent No. 4,521,387 catalyses the water gas shift reaction in presence of carbon dioxide and steam.

The general object of this invention is thus to improve the known processes for selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and further containing both hydrogen, carbon dioxide and optionally steam.

It has been found that an absorbent of reduced Cu/ZnO/Al₂O₃ removes H₂S and COS to below 5 ppb levels in such a synthesis gas with high sulphur capacity. It has also been observed that methanol synthesis does not occur at 40°C or at 125°C and that conversion of CO through the water gas shift reaction is absent at 100°C or below.

Useful absorbents comprise Cu/ZnO compounds, e.g. prepared by thermal decomposition of the respective salts and carbonates, and subsequent activation with reducing gas (e.g. H₂/N₂) and compositions of copper on ZnO carrier.

In accordance with the above object and observations, this invention is a process for the selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and containing hydrogen and carbon dioxide comprising contacting the synthesis gas at a maximum contact temperature of 125°C with an absorbent comprising Cu/ZnO compounds being activated with a reducing gas.

When operating the invention with wet synthesis gas, the maximum contact temperature is 100°C.

An advantage of the reduced copper based absorbents, in which copper metal is active, is the ability to remain stable in synthesis gas rich in carbon monoxide even if exposed to higher temperatures.

In addition to absorption of H₂S, reduced copper based absorbents are effective absorbents in removing COS, being formed by side-reactions,



in the absorber or up-stream the absorber at certain process conditions.

In further an embodiment of the invention the absorbent is useful to remove sulphur being added to synthesis gas to

suppress metal dusting in chemical plants, as described in more detail below.

5 Metal dusting corrosion is a well-known phenomenon in the chemical industry described in numerous publications. Metal dusting corrosion involves disintegration of metals and alloys into small particles of metal, metal carbides, metal oxides and carbon.

10 A key element of metal dusting is the transfer of carbon from the gas phase to the metal or alloy.

15 Affinity for carbon formation decreases with increasing temperatures. The temperature below which is affinity for carbon precipitation is called the Boudouard temperature. Typical Boudouard temperatures are in the range up to 1000°C.

20 Carbon monoxide is the predominant cause of metal dusting corrosion, but hydrocarbons have also been reported to cause metal dusting.

25 For kinetic reasons metal dusting only proceeds significantly at temperatures above a certain level, typically more than 300°C.

The metal dusting corrosion phenomenon is thus observed predominantly in the temperature range of 300°C to 1000°C.

30 It is known that metal dusting is suppressed by the presence of H₂S in carbon monoxide containing gas. Meanwhile,

H_2S is poisonous to down-stream catalysts, H_2S content of the gas must be maintained at a very low level of 5 ppb.

In a number of industrial processes it is possible to use 5. H_2S as protecting agent against metal dusting, if the down-stream processes accepts sulphur compounds or if the synthesis gas is passed through a CO_2 removal unit, wherein 10. also H_2S is removed. In the latter case a failure in operation of the CO_2 removal unit will cause irreversible inactivation of down-stream catalysts, if these are susceptible 15. to sulphur poisoning.

Thus, in a specific embodiment of the present invention, 15. H_2S is added to the synthesis gas up-stream to equipment being subjected to metal dusting, and subsequently selectively removed down-stream to the equipment.

In case the synthesis gas preparation section is tolerant 20. to sulphur, the natural contents of sulphur in the hydro-carbon feed reformed is not removed and optionally supplementary H_2S may be added at any position upstream the equipment subjected to metal dusting to provide H_2S concentration in the synthesis gas being effective for the suppression of metal dusting down stream the reformer. H_2S is 25. then selectively removed downstream to the equipment.

Thus, in another aspect the invention provides use of the 30. adsorbent in the suppression of metal dusting of iron or nickel alloys in contact with carbon monoxide rich synthesis gas at a Boudouard temperature above 300°C, further containing both hydrogen, carbon dioxide and optionally steam. Thereby an amount of a H_2S source is added to the

synthesis gas upstream the metal surface being in contact with the gas in a concentration being sufficient to suppress metal dusting. Subsequently the sulphur compound is selectively removed at a temperature below 125°C downstream 5 the metal surface.

The H₂S source may be either a gas containing H₂S or another sulphur compound, which at actual process conditions will decompose into H₂S, e.g. dimethyl disulphide.

10 The examples below demonstrate in more detail specific embodiments of the invention.

Example 1

15 Reference is made to Fig. 1. In this specific embodiment of the invention Fe and Ni containing alloys being exposed to synthesis gas downstream an autothermal reformer are protected against metal dusting. The synthesis gas produced in 20 an autothermal reformer is well suited for the synthesis of synthetic liquid fuel in a down stream Fisher-Tropsch synthesis section.

25 The synthesis gas exiting an autothermal reformer (100) at 30 bar gauge contains by volume percent approximately H₂ 49, H₂O 20, CO 25, CO₂ 5 and CH₄ 1 corresponding to a Boudouard temperature of approximately 900°C. Potentially metal dusting will occur on Fe/Ni alloy surfaces between 300°C and 900°C if not protected.

30 CH₃SSCH₃ (110) is added to the synthesis gas effluent from the autothermal reformer. At the high temperature prevail-

ing the CH_3SSCH_3 will thermally decompose and react with H_2 into H_2S . The amount of CH_3SSCH_3 added corresponding to approximately 1 ppm H_2S by volume in the resulting admixture (120).

5

The admixture is led through a series of heat exchange operations, where it during cooling supplies heat to other processes or streams. The first heat exchange operation (130) is a gas heated heat exchange reformer which receives 10 heat from the admixture, while the admixture cools from 1050°C to approximately 600°C. The effluent from the gas heated heat exchange reformer (130) can in another lay-out be added to the synthesis gas from the autothermal reformer. The second heat exchange operation (140) is a 15 boiler for steam production which receives heat from the admixture, while the admixture cools from 600°C to approximately 300°C. During cooling of the admixture in the heat exchange operations (130) and (140) Fe and Ni containing 20 alloys being exposed to the synthesis gas trans-passes a temperature range 700-500°C, wherein severe metal dusting is observed. H_2S contained in the admixture protects heat recovery equipment against metal dusting down to a temperature of 300°C, where metal dusting for kinetic reasons does 25 no longer occur. Under the kinetic limit for metal dusting heat recovery equipment is protected by low operating temperature and H_2S is no longer needed for this purpose. The third heat exchange operation (150) is a boiler feed water preheater which receives heat from the admixture, 30 while the admixture cools from 300°C to approximately 100°C. After the heat exchange operation (150), which brings the admixture to below the dew point of water, a first separation of process condensate is made (160). The

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fourth heat exchange operation (170) is a second boiler feed water preheater which receives heat from the admixture, while the admixture cools from 100°C to approximately 40°C. After the heat exchange operation (170), separation of process condensate is again made (180). The saturated synthesis gas outlet of the last process condensate separation (180) is brought to conditions above the dew point of water contained in the synthesis gas, in this example by simply re-heating of the synthesis gas in the heat exchange operations (190) and (200). This re-heating must be done in case the downstream absorbent is susceptible to hydration.

Re-heated synthesis gas is introduced to a bed of sulphur absorbent (210), removing sulphur to a level below 5 ppb, acceptable to most down stream syntheses.

Example 2

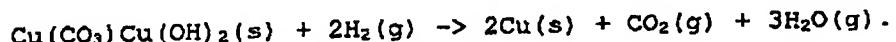
This Example is not an example of the present invention. It illustrates the ease of reduction of mixed basic carbonates exposed to a typical synthesis gas.

108 mg of mixed basic carbonates were loaded into a thermogravimetric reactor. In such a reactor the weight of the sample is continuously recorded. The reactor operates at atmospheric pressure. The sample was exposed to reducing gas with the composition by volume percent H₂ 66.6 (balance), H₂O 2.2, CO 18.4, CO₂ 9.8 and Ar 3.0 for approximately 6 days at 45°C. Then the temperature was raised to 55°C and the experiment was run for another approximately 5 days.

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Fig. 2 shows that at 45°C the weight of the sample of mixed basic carbonates is stable. Any reduction of mixed basic carbonates of copper would be accompanied by a weight loss through the reaction

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The mixed basic carbonates are not reduced by synthesis gas at 45°C.

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In line with the above reduction is seen, as a slowly decreasing weight, when the temperature is increased to 55°C.

Comparison Example 3

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A test was made on desulphurisation of a synthesis gas at conditions typical of the outlet of the process condensate separation. The test was made on pure ZnO, more specifically on the catalyst type HTZ-3 available from Haldor Topsoe A/S, Denmark.

20

The test was carried out at accelerated conditions with a space velocity of approximately 10 times higher than a typical industrial space velocity and with a concentration of H₂S of approximately 5 times higher than what is needed to obtain a pronounced suppression of metal dusting corrosion.

25

Catalyst particles in the form of 4 mm cylinders were loaded in a plug flow reactor with an internal diameter of 5 mm. Thereafter, the test conditions were as follows:

Temperature 40°C
Pressure 20 bar gauge
Space velocity 25,000 Nm³ gas/m³ catalyst/h

5 Gas composition, percent by volume H₂ 72.4 (balance), H₂O 0.02(approximately), CO 14.6, CO₂ 10.0, Ar 3.00, H₂S 3.8 ppm by volume, COS 100-200 ppb by volume.

10 The results of the test are shown in Fig. 3, where the outlet concentration of H₂S and COS are given versus the time on stream. Breakthrough of sulphur is seen already after about 50 hours of operation. Pure zinc oxide is, thus, not suitable for this kind of desulphurisation.

15 **Example 4**

This is an example of the present invention, as a reduced Cu/ZnO compound has been used for the desulphurisation of synthesis gas rich in carbon monoxide and further containing both hydrogen and carbon dioxide.

20 Example 3 was repeated, however, reduced Cu/ZnO/Al₂O₃ was used as absorbent instead of ZnO, more specifically the catalyst type ST-101 available from Haldor Topsoe A/S, Denmark. The ST-101 was reduced prior to the test.

25 The results of the test are shown in Fig. 4, where the outlet concentration of H₂S and COS are given versus the time on stream. For Cu/ZnO/Al₂O₃ desulphurisation to the required low ppb level (5ppb) is obtained for about 200 hours, whereafter a breakthrough of COS is seen. Methanol synthesis was absent also during a short time test at 125°C after 66 hours of operation. When the test was terminated af-

5 ter 300 hours, H₂S was still below the detection limit of 5 ppb. The experiment was as mentioned before conducted with 10 times the normal space velocity and at 5 times the required H₂S level. Therefore an estimated operation time for an industrial application will be at least 50 times the experimental run time. Thus, 200 hours of desulphurisation to below detection limit of COS and H₂S corresponds to 10000 hours of industrial operation below detection limit, which makes the process industrially useful.

10 Formation of COS can be explained by absorbed H₂S being converted by carbon monoxide in the feed gas to COS and hydrogen.

15 **Example 5**

20 This Example relates to whether the reduced Cu/ZnO compound catalyses the water gas shift reaction at the desulphurisation temperatures. The Cu/ZnO compounds are known to be excellent water gas shift catalysts. Therefore, it is important for the present invention to establish how low the desulphurisation temperature should be in order to limit the conversion of CO through the water gas shift reaction to insignificant levels.

25 The conversion of CO, through the water gas shift reaction, is possible because the synthesis gas to be desulphurised often is saturated with water and because the thermodynamic affinity for water gas shift, being an exothermic reaction, 30 is large at low temperatures.

Considering the conditions of Example 1 the synthesis gas leaving the first water separator at 100°C will contain approximately 3% by volume of water. Therefore, the water gas shift reaction, in case it was catalysed by the sulphur absorbent, could lead to a large loss of CO from the synthesis gas.

The test on the water gas shift reaction was made on a Cu/ZnO/Al₂O₃ absorbent, more specifically the catalyst ST-101 available from Haldor Topsøe A/S, Denmark. Catalyst particles in the form of approximately 4 mm cylinders were loaded in a plug flow reactor with an internal diameter of approximately 8 mm. The catalyst was reduced, and thereafter the test conditions were as follows:

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Temperature 148, 125 and 110°C
Pressure 20 bar gauge
Space velocity 5400-8500 Nm³/m³ catalyst/h

20 Dry gas composition, percent by volume:
H₂ 72.50 (balance), CO 14.5, CO₂ 10.0, Ar 3.0

Steam to dry gas ratio, volume to volume: 0.028 - 0.090

25 At 148°C and 125°C a significant conversion of CO through the water gas shift reaction was observed. At 110°C conversion was hardly to be observed any more.

30 By extrapolation of the test results it shows that at 100°C and at a typical industrial space velocity of 2500 Nm³/m³ catalyst/h, the conversion of CO will be only a fraction of

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a per thousand. In other words, and for practical purposes, the Cu/ZnO/Al₂O₃ absorbent does not catalyse the water gas shift reaction at 100°C or below.

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CLAIMS

- 1.. A process for the selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and containing hydrogen and carbon dioxide comprising contacting the synthesis gas at a maximum contact temperature of 125°C with an absorbent comprising Cu/ZnO compounds being activated with a reducing gas.
5
- 10 2. Process of claim 1, wherein the synthesis gas further contains steam and the maximum contact temperature is 100°C.
- 15 3.. Process of claims 1 or 2, wherein the sulphur compounds comprise H₂S and COS.
- 20 4. Process according to any one of the preceding claims, wherein the synthesis gas contains H₂S in an amount effective for suppression of metal dusting of metals in contact with the synthesis gas within a temperature range between 300°C to Boudouard temperature of the synthesis gas.

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ABSTRACT

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5 A process for the selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and containing hydrogen and carbon dioxide comprising contacting the synthesis gas at a maximum contact temperature of 125°C with an absorbent comprising Cu/ZnO compounds being activated with a reducing gas.

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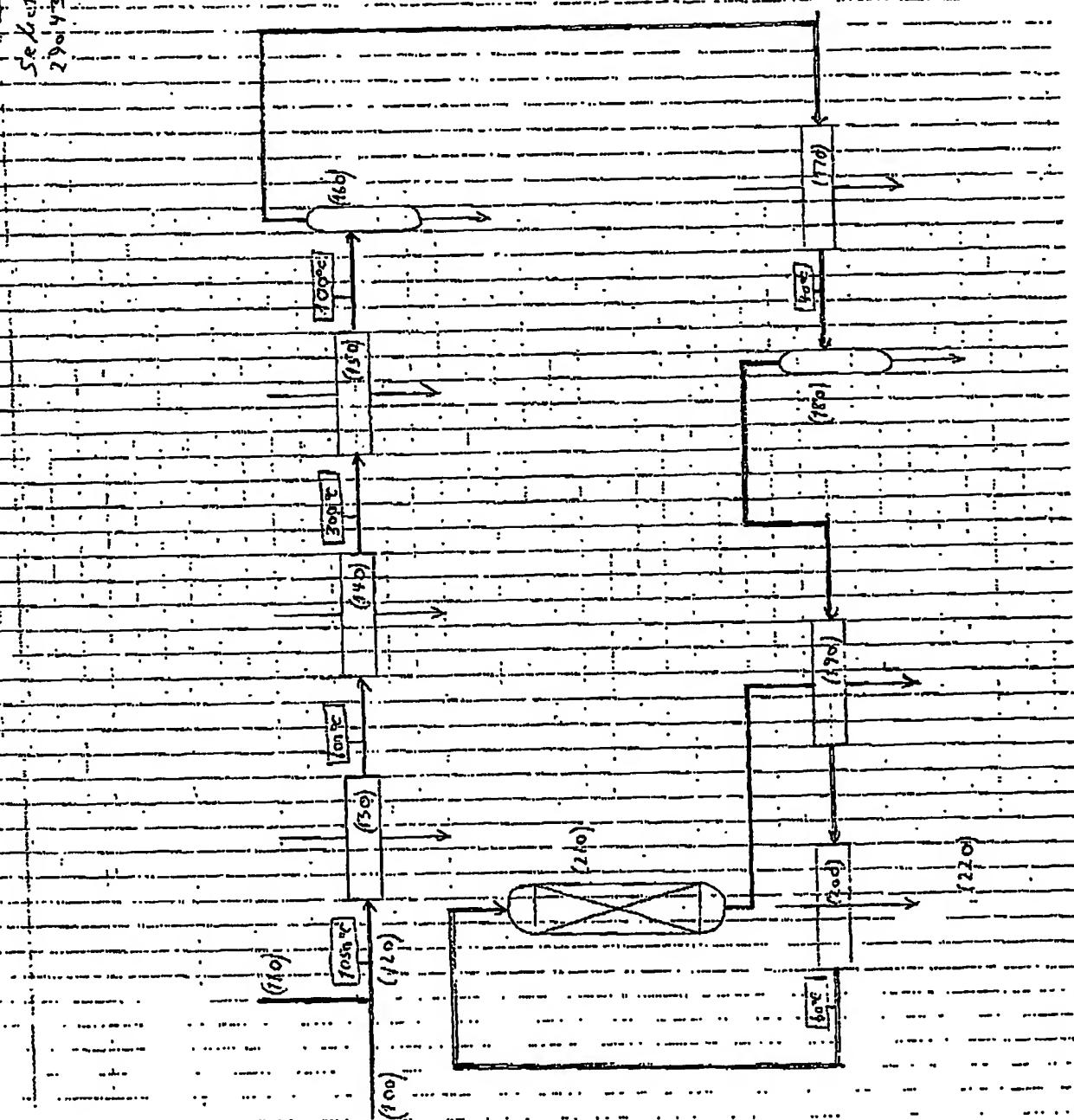
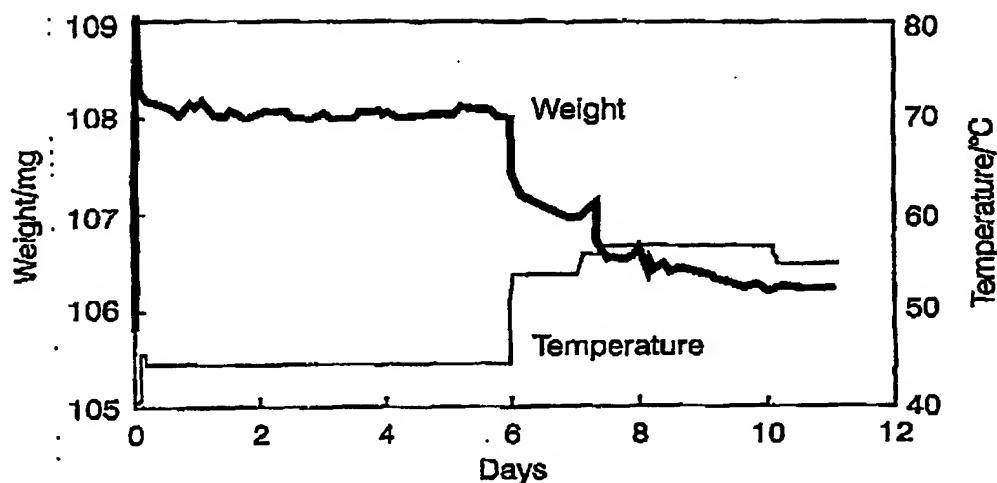


FIG. 1

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Temperature programmed reduction of mixed basic carbonates

FIG. 2

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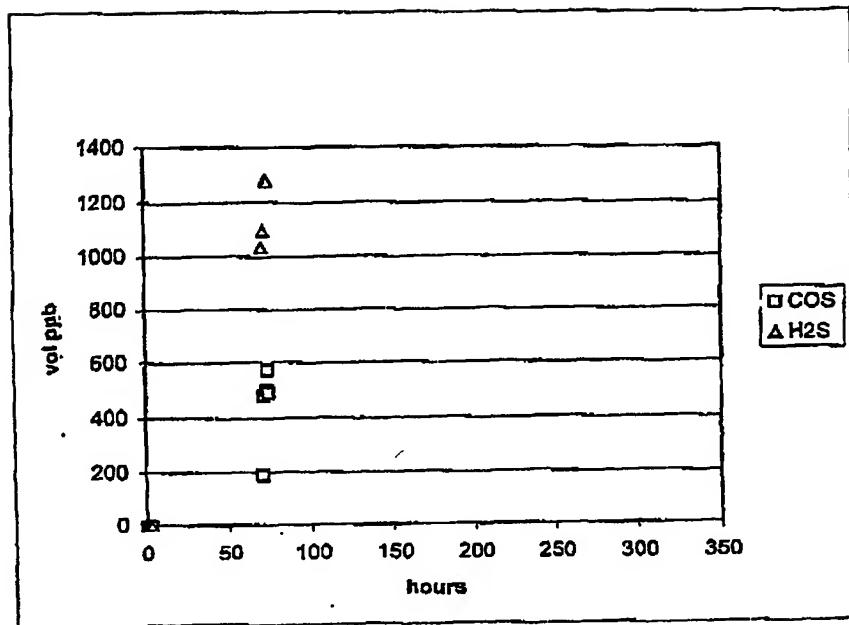
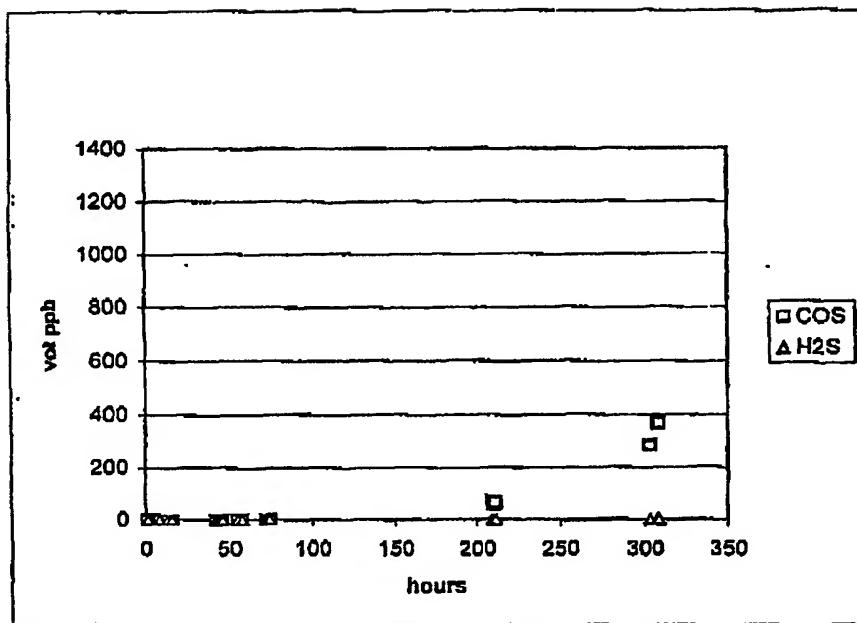


FIG. 3

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Absorption of sulphur at 40°C and 21 bar
on Cu/ZnO/Al₂O₃

FIG. 4

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